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MEASUREMENT OF NON-METHANE HYDROCARBONS

Contract CPA 70–40
SwRI Project 21–2811

Prepared for:

Office of Measurement Standardization
Division of Chemistry and Physics
Air Pollution Control Office
Environmental Protection Agency

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16. Abstracts

Measurement of so-called "non-methane hydrocarbons" has been carried out in a mobile laboratory using a flame ionization detector. Total hydrocarbons were measured by running air directly through the detector. Methane was measured by running air through a methane-saturated carbon column which retained all organic contaminants other than methane. The difference was then the "non-methane hydrocarbons." Two methods of measurement were used: (1) The air stream was diverted alternately through the detector or through the carbon column and then the detector; the total hydrocarbon measurement for several consecutive cycles was averaged, and the methane measurement for comparable cycles was averaged; the difference was then the measure of non-methane hydrocarbons for the entire period. (2) Air was admitted to a plastic bag over a period of time, after which the total hydrocarbon and methane content of the collected sample was determined; again, the difference was the non-methane hydrocarbon value for the sampling period. Temperature control of the carbon adsorbent is important and may be critical. Temperature variations during sampling affect the methane capacity of the carbon, causing errors in measurement. Service life of the carbon is short for a continuous monitoring instrument. Increasing the amount of carbon increases service life, but also increases time lag and decreases response time of the instrument. Also, increasing the amount of carbon increases the possible error due to temperature variations. Bag sampling may be superior to continuous monitoring, depending on circumstances. One instrument can analyze samples collected at a number of monitoring stations. Careful purging of plastic bags is required to avoid errors due to desorption of organic constituents of the plastic. Sensitivity appears to be marginal in view of the federal standards. The method is subject to error due to difficulties in calibration, temperature control, and other variables. Therefore, good results can be obtained only by well trained and experienced personnel.

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by

Oscar Saenz, Jr.
Clarence A. Boldt, Jr.
David S. Tarazi

June, 1971

APPROVED BY:

Herbert C. McKee

Herbert C. McKee
Assistant Director
Department of Chemistry
and Chemical Engineering

SOUTHWEST RESEARCH INSTITUTE
3600 YOAKUM HOUSTON, TEXAS 77006

SUMMARY AND CONCLUSIONS

Measurement of so-called "non-methane hydrocarbons" has been carried out in a mobile laboratory using a flame ionization detector. Total hydrocarbons were measured by running air directly through the detector. Methane was measured by running air through a methane-saturated carbon column which retained all organic contaminants other than methane. The difference was then the "non-methane hydrocarbons."

Two methods of measurement were used:

(1) The air stream was diverted alternately through the detector or through the carbon column and then the detector. The total hydrocarbon measurement for several consecutive cycles was averaged, and the methane measurement for comparable cycles was averaged; the difference was then the measure of non-methane hydrocarbons for the entire period.

(2) Air was admitted to a plastic bag over a period of time, after which the total hydrocarbon and methane content of the collected sample was determined. Again, the difference was the non-methane hydrocarbon value for the sampling period.

The following conclusions resulted from this work:

1. Temperature control of the carbon adsorbent is important and may be critical. Temperature variations during sampling affect the methane capacity of the carbon, causing errors in measurement.

2. Service life of the carbon is short for a continuous monitoring instrument. Increasing the amount of carbon increases service life, but also increases time lag and decreases response time of the instrument. Also, increasing the amount of carbon increases the possible error due to temperature variations.

3. Bag sampling may be superior to continuous monitoring, depending on circumstances. One instrument can analyze samples collected at a number of monitoring stations. Careful purging of plastic bags is required to avoid errors due to desorption of organic constituents of the plastic.

4. Sensitivity appears to be marginal in view of the proposed (and recently revised and adopted) federal standards.

5. The method is subject to error due to difficulties in calibration, temperature control, and other variables. Therefore, good results can be obtained only by well trained and experienced personnel.

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I. INTRODUCTION

The method in use at Southwest Research Institute to measure non-methane hydrocarbons is a combination of two methods entitled "Continuous Analysis of Methane" and "Tentative Method for the Continuous Measurement of Total Hydrocarbons in the Atmosphere" (Flame Ionization Method). These methods were obtained from EPA-APCO for evaluation.

The analysis of methane is carried out by passing the ambient sample continuously through an activated charcoal sorption tube which adsorbs all organic contaminants except methane. The methane is then analyzed by a flame ionization instrument. The column is no longer usable when heavier organic compounds begin to elute. For this reason, a close check has to be performed on the scrubber column periodically.

The total hydrocarbons, on the other hand, are analyzed with a flame ionization instrument without the charcoal column. The difference between the measured total hydrocarbons and methane represents the non-methane hydrocarbons.

II. DESCRIPTION OF SYSTEM

A Beckman Model 109-A Total Hydrocarbon Analyzer was modified in order to make it capable of analyzing both parameters consecutively and automatically. The flow system of the instrument is shown in Figure 1. A programmer has been installed that allows the instrument to sample automatically in the following time sequence:

Step 1	- zero	1 minute
	2 - total hydrocarbons	5 minutes
	3 - zero	1 minute
	4 - methane	5 minutes

This sequence can run repetitively as long as desired. At the end of the sampling period, the recorder (strip chart) data for the total hydrocarbons and the methane as shown in Figure 2 are read and averaged. The difference of these averages represents the average non-methane hydrocarbons over a unit period of time.

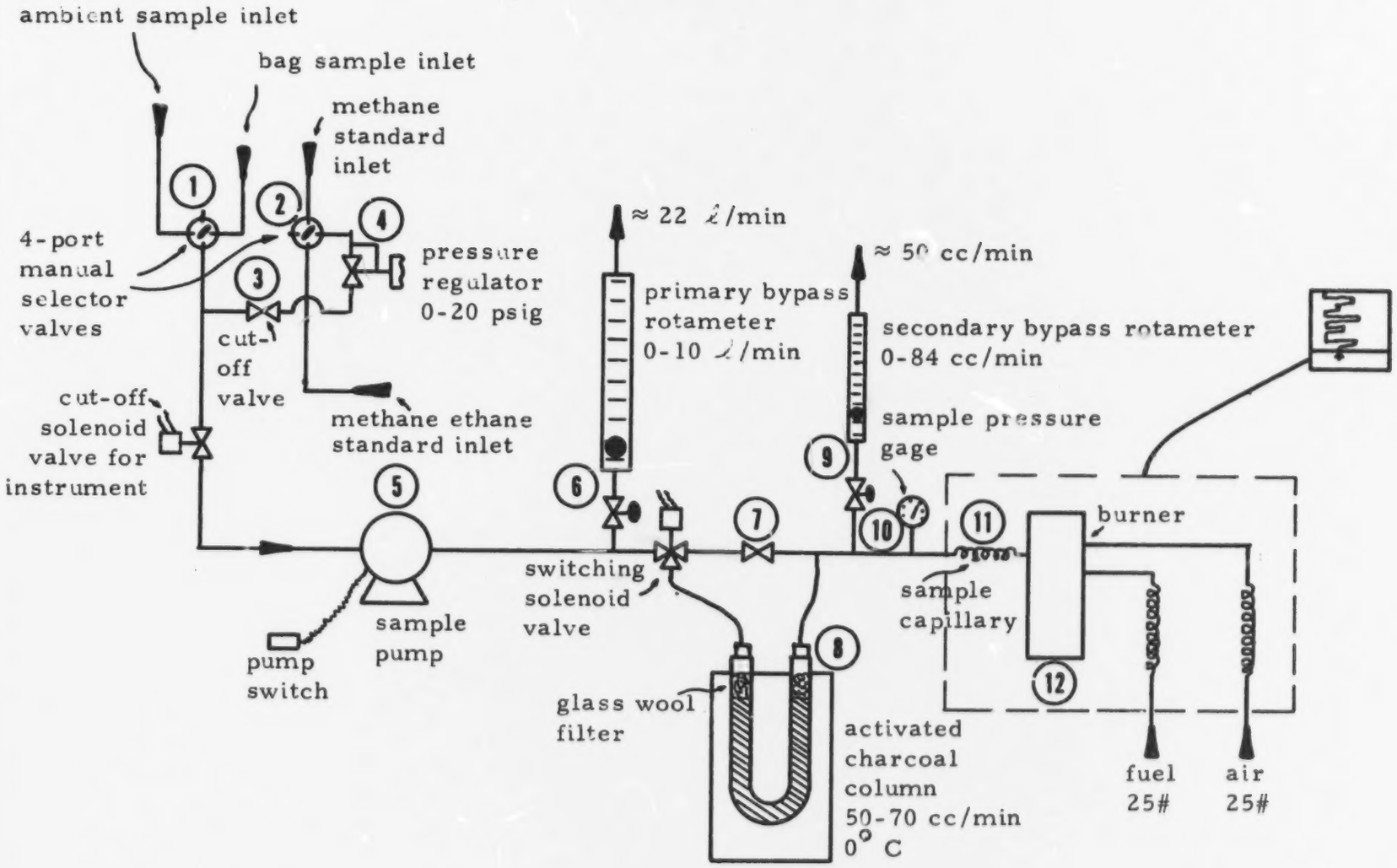
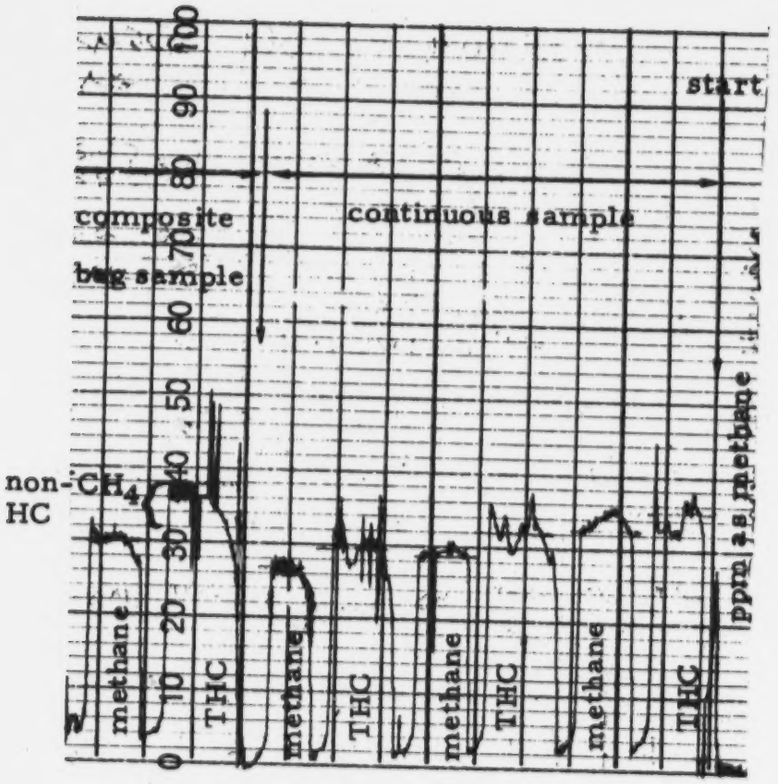


Figure 1. Flow System for Total Hydrocarbon and Methane Analyzer Using Beckman Model 109-A Analyzer



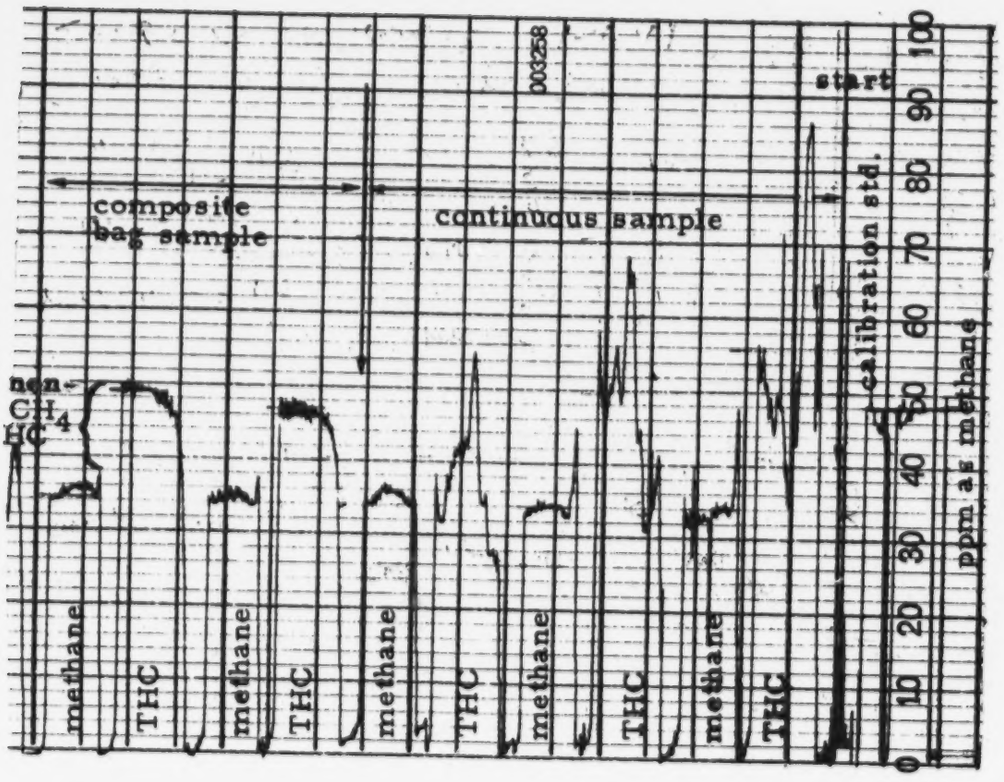


Figure 2. Typical Strip Chart Recordings of Total Hydrocarbons and Methane on Ambient Samples Taken Near Industrial Site

III. COLUMN

The carbon sorption column used in the instrument consists of a 10" long x 1/2" ID glass U tube packed with 5-10 grams of Burrell's high activity chromatographic grade charcoal. This charcoal was purchased from Curtin Scientific Company. As shown in Figure 1, the column is attached in parallel to a bypass column through a solenoid valve. This solenoid valve, which serves as a switching device, is connected to the programmer. The adsorbent may be preheated 6-12 hours at 120^{o} C prior to use. It is not necessary to condition it with methane prior to its use as will be explained later. The flow of ambient air through the column is maintained at a rate of 50-60 cc/min.

IV. ADSORBENT EVALUATION

Before selecting the charcoal presently used in the system, various brands and types of charcoal were investigated. The evaluation was performed in the laboratory with the aid of a Perkin-Elmer Model 900 gas chromatograph equipped with a flame ionization detector. Five and ten grams of each brand of charcoal were packed into glass U tubes, as previously described, and evaluated one at a time. A prepared gas mixture, containing 5 ppm methane and 2 ppm ethane, was passed continuously through the column and through a gas sampling valve in the gas chromatograph at a flow rate of 50-60 cc/min. The columns were evaluated at 0° C and 25° C for adsorption efficiencies. Eluent samples were introduced into the gas chromatograph at "0" time and time intervals thereafter through the gas sampling valve. The gaseous mixture was analyzed by making a separation of the methane and ethane components in the normal gas chromatographic technique by using a 5" x 1/4" OD silica gel column or a 5" x 1/8" Porapak Q column as shown in Figures 3 and 4, respectively. By employing this technique, data were obtained showing the exact time methane and ethane "broke through" the charcoal columns. The time at which ethane "broke through" represents the life duration of the column under the conditions investigated.

After it was determined that Burrell's high activity charcoal was more efficient than the other charcoals under the conditions investigated, various experiments were performed. These experiments were run for the purpose of determining the adsorption capacity of the activated charcoal for ethane at 0° C and 25° C. As expected, the results showed a higher adsorption efficiency at the lower temperature. This is illustrated in Figures 5 through 7 and summarized in Figure 8, which is a plot of data showing the loading characteristics of the Burrell high activity charcoal for 2 ppm ethane at 0° C and 25° C. This figure clearly illustrates that when the adsorption temperature is kept at 0° C, the charcoal which has not been preheated adsorbs almost four times as much ethane as compared to the amount adsorbed at a temperature of 25° C. Based on these findings, the column on the instrument used at SwRI is always maintained at 0° C by placing the column in an ice bath.

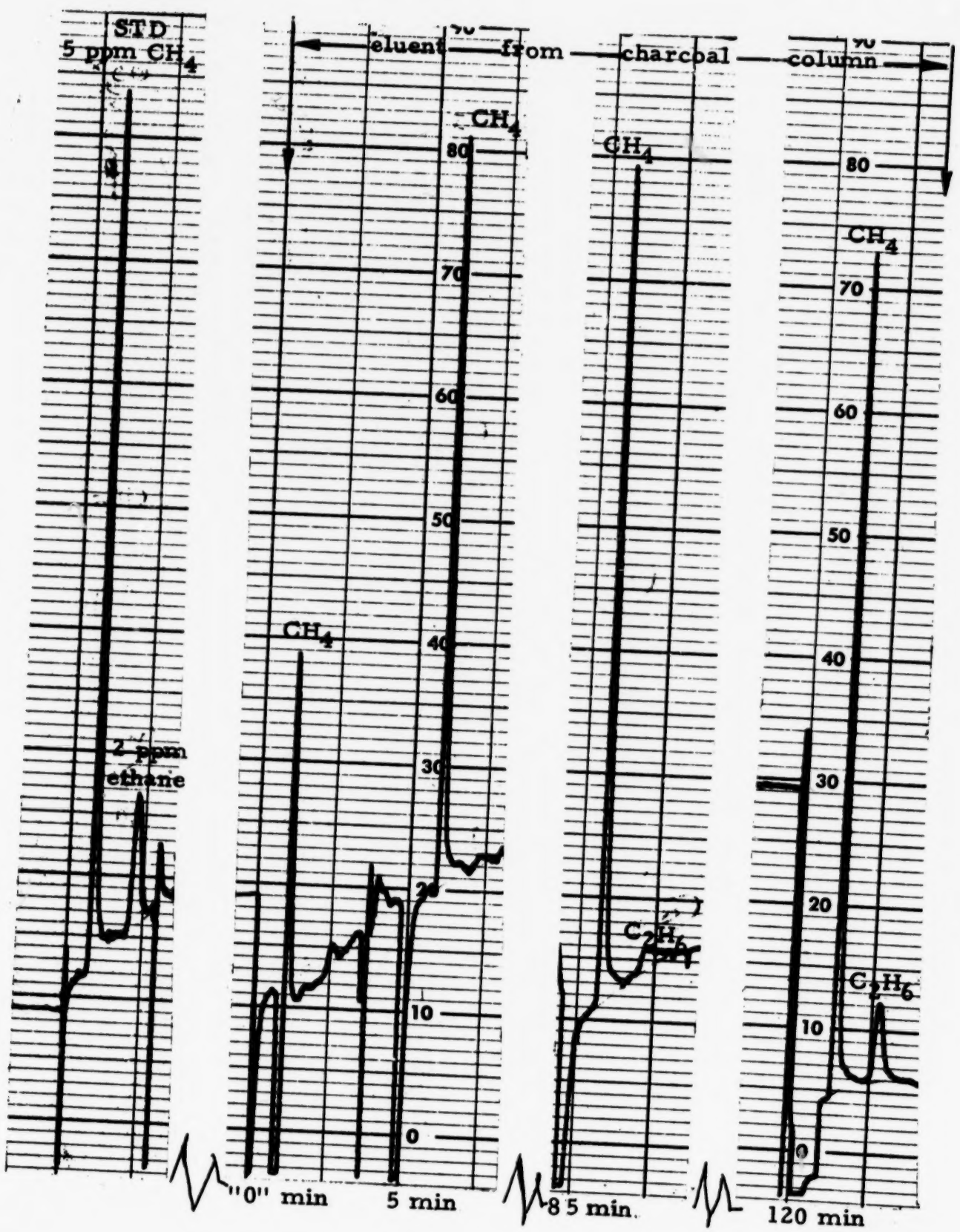


Figure 3. Evaluation of Activated Charcoal by Gas Chromatography (Separation Made on Silica Gel Column)

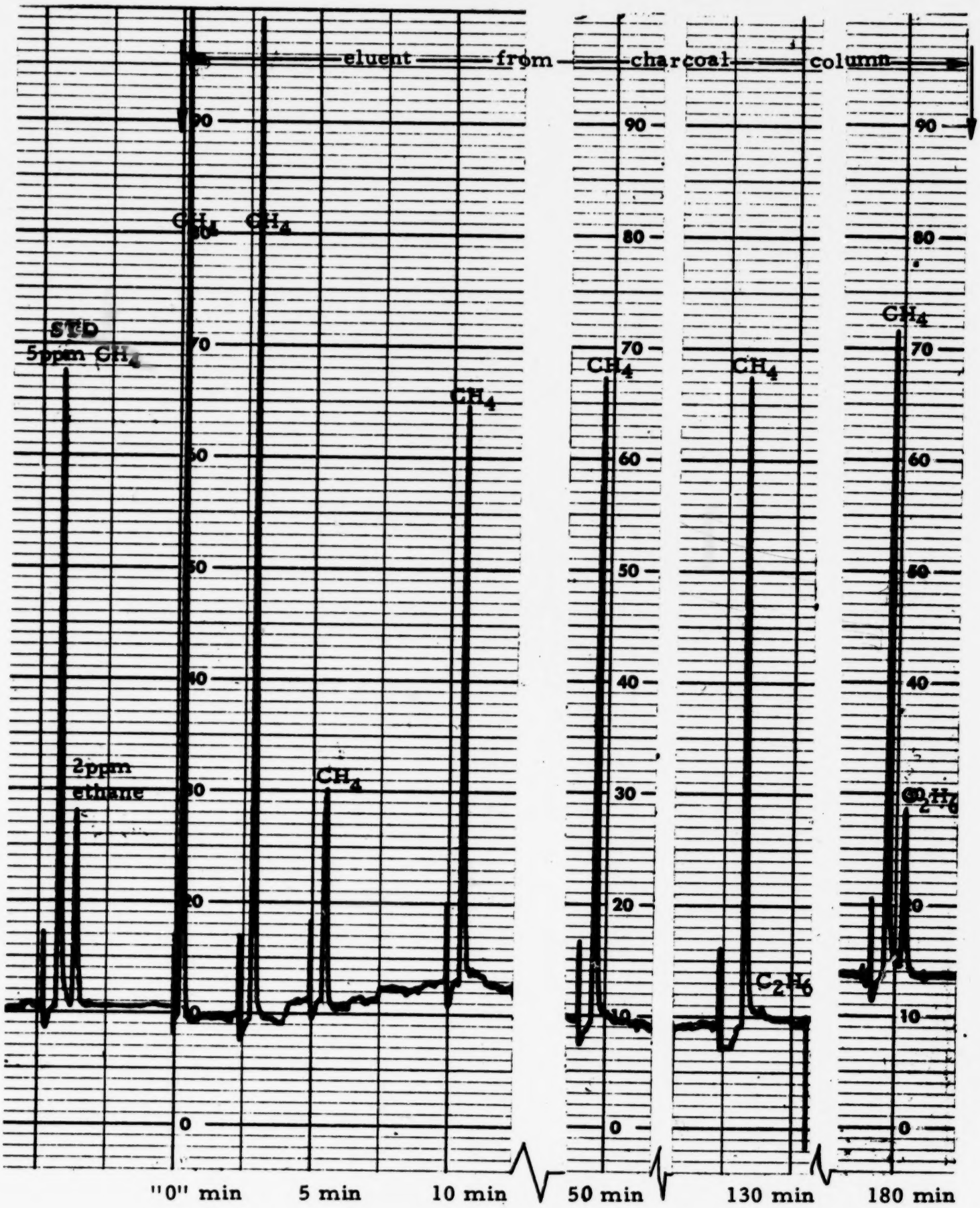


Figure 4. Evaluation of Activated Charcoal by Gas Chromatography
(Separation Made in Porapak Q Column)

Figure 5. Adsorption of Methane and Ethane by Activated Charcoal at 25° C (Charcoal not Preheated)

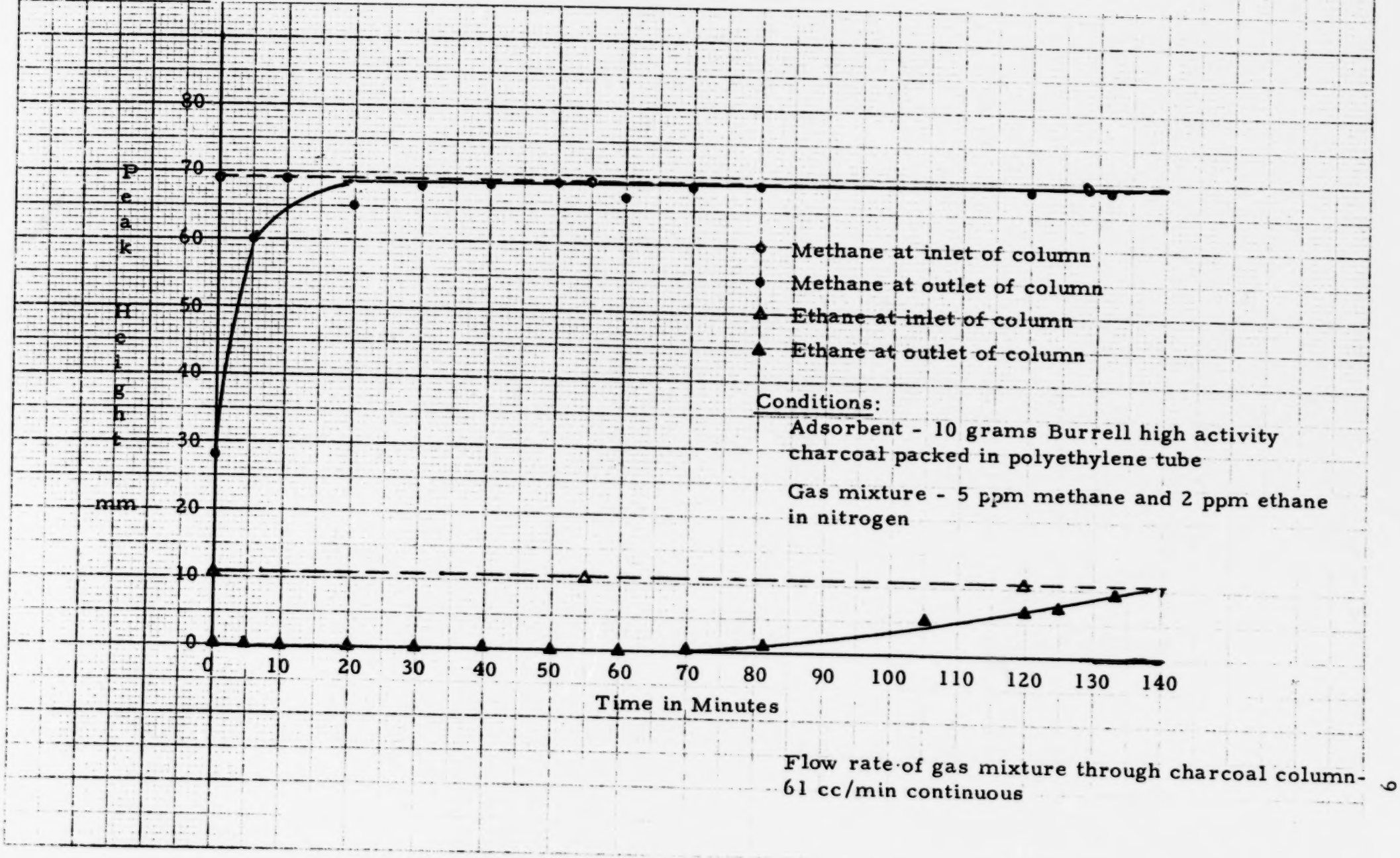
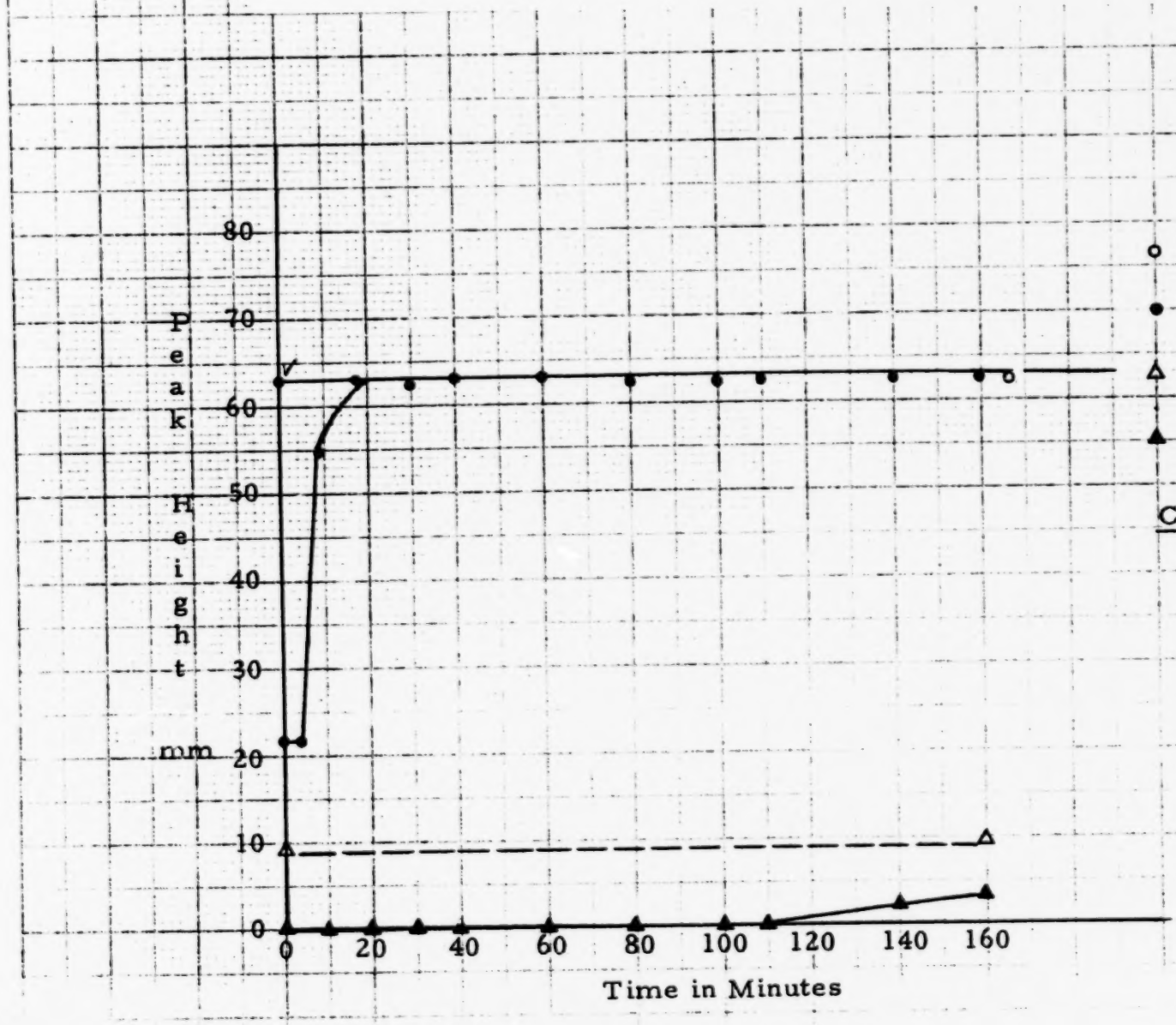


Figure 6. Adsorption of Methane and Ethane by Activated Charcoal at 25° C
(Charcoal Preheated)



Conditions:

Adsorbent - 10 grams Burrell high activity charcoal preheated 6-8 hr at 120° C prior to use packed in polyethylene tube

Gas mixture - 5 ppm methane and 2 ppm ethane in nitrogen

Flow rate of gas mixture through column - 61 cc/min continuous

Figure 7. Adsorption of Methane and Ethane by Activated Charcoal at 0° C

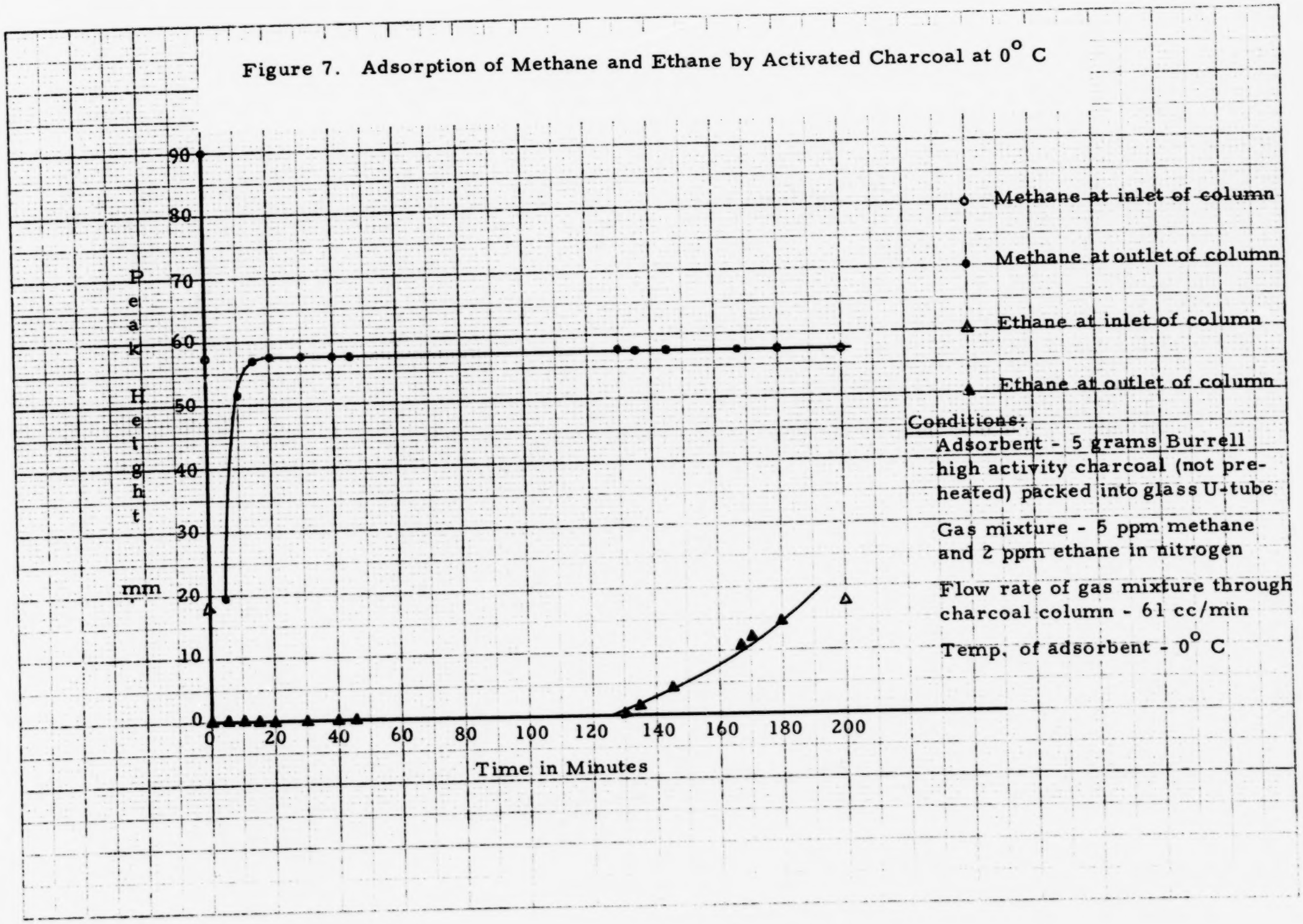


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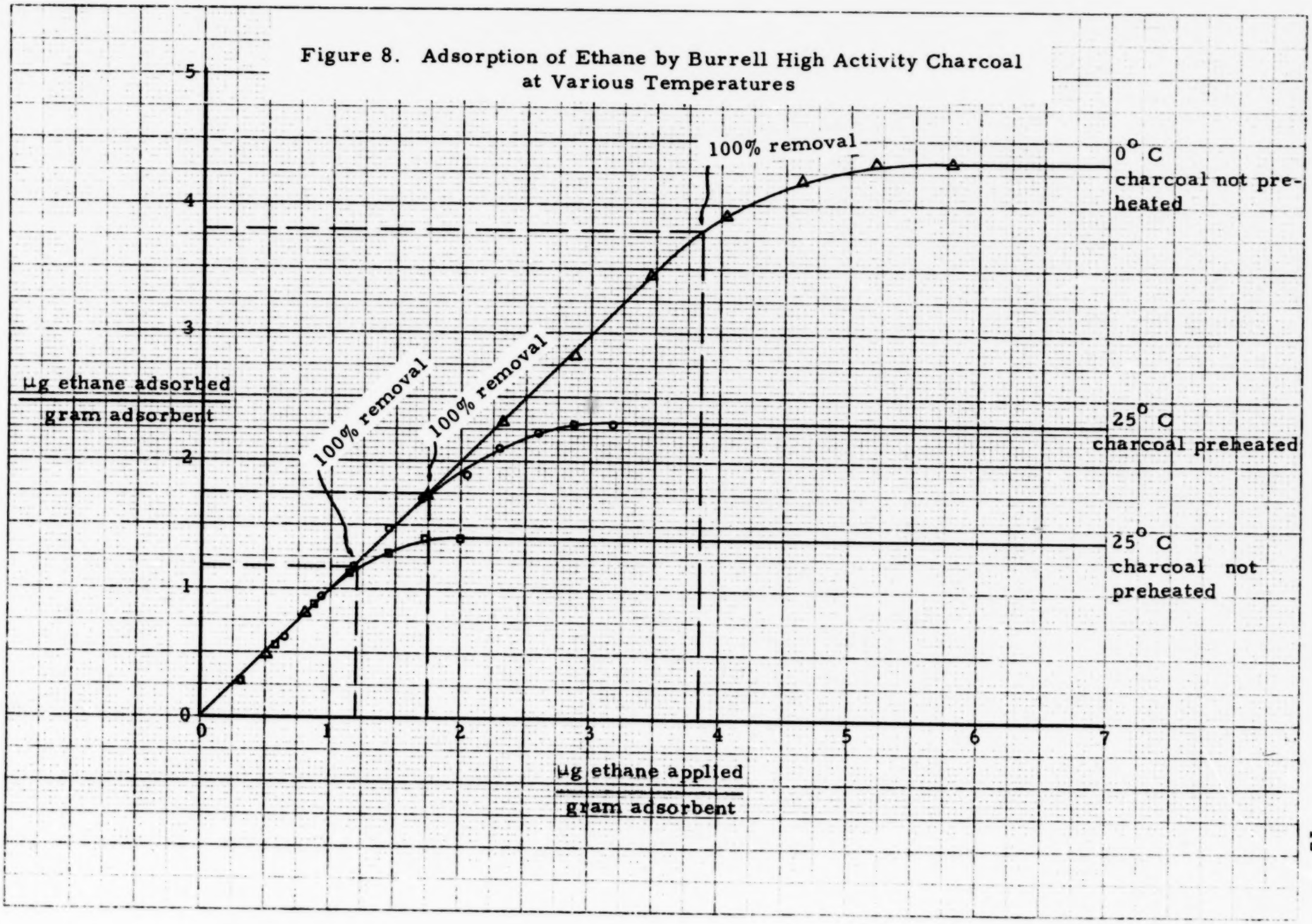
Figure 8. Adsorption of Ethane by Burrell High Activity Charcoal at Various Temperatures



V. OPERATION OF THE ANALYZER

The "start-up" procedure for the Beckman Model 109-A Total Hydrocarbon Analyzer will not be discussed since this information can be obtained from the manufacturer's handbook. The following discussion on the calibration and sampling techniques of the modified instrument whose flow schematic is shown in Figure 1 assumes that the instrument has been started and ample warm-up time has been allotted.

VI. CALIBRATION PROCEDURE

Prior to ambient sampling, the analyzer is calibrated by continuously flowing a methane standard (1-10 ppm CH_4 in air) into the instrument. It is necessary to determine the ΔP (flow) across the instrument sample capillary in order to obtain a recorder response which can be related to the concentration of methane in the calibration gas.

The procedure for calibrating the analyzer is as follows: (Refer to Figure 1.)

1. Turn off the sample pump (5) and shut off needle valve on primary bypass (6). The bypass valve and the flowmeter, which will be described later, are used only during ambient sampling.

2. Place selector valves (1) and (2) in the proper position to allow the std methane cylinder to be placed in line. Turn second stage on cylinder regulator to show 0-5 psi, and close pressure regulator (4). This regulator serves as a third stage of reduction and will be used to control flow of calibration gas through the system.

3. Turn instrument programmer to total hydrocarbon manual mode. This position allows the calibrating gas to bypass the charcoal column (8) through bypass (7). During calibration, the standard gas does not flow through the charcoal column.

4. After zeroing the instrument electronically, as described in manufacturer's manual, open cutoff valve (3). This valve allows the calibration standard to be introduced into system.

5. Adjust pressure regulator (4) to allow standard gas to flow. Observe flowmeter (9) which indicates flow rate of the standard gas through the bypass (7). The regulator should be adjusted to indicate a flow not to exceed 70 cc/min. This flowmeter (9) is used in the instrument primarily as a splitter, since the sample capillary tube (11) cannot stand a high flow through the detector. Consequently, only a small portion of the total flow goes through the detector.

6. Continue adjusting pressure regulator (4) slowly until a stable and desired response is observed on the instrument recorder. Once the desired response is achieved, record the ΔP observed on the sample pressure gage (10), which indicates the flow across the sample capillary. The value obtained represents the calibration point which will be used when performing the ambient sampling.

7. Turn off cutoff valve (3), and return selector valves (1) and (2) to ambient sampling mode. The instrument is now ready for ambient sampling.

VII. AMBIENT SAMPLING

1. After the selector valves have been placed in the ambient mode position and the programmer placed in the zero (manual) position, turn on the sample pump (5). Readjust the zero on the instrument meter and recorder.

2. Slightly open the primary bypass valve (6). This valve is used as a primary sample splitter. Its purpose is to bypass the majority of the total flow delivered by the sample pump (5). This extremely large flow, about 5-8 ℓ/min, is undesirable since it will rapidly load the charcoal column and thus decrease its life duration. As mentioned previously, only a flow not to exceed 70 cc/min can be tolerated through the column.

3. Turn programmer to CH_4 manual mode. This allows the ambient sample to flow through the charcoal column (8) which has been immersed in an ice bath and maintained at 0° C.

4. The primary bypass valve (6) which controls the flow through the system is then adjusted to obtain a reading on the sample pressure gage (10) which is identical to the calibration value point.

5. After Step 4 has been accomplished, the programmer is then manually moved to the THC mode, which allows the sample to flow through the bypass column (7) and into the detector. The flow is again adjusted as was done in Step 4 to obtain the calibration value on the sample pressure gage (10). However, this flow is adjusted this time with a needle valve found on the bypass (7). This valve simulates a pressure drop across the bypass equal to the ΔP across the charcoal column.

6. The instrument is now ready to perform ambient sampling. The sampling sequence is then started by placing the programmer in the zero mode position. This position activates the cutoff solenoid which in turn cuts off the sample flow, thus allowing the zeroing of the instrument electronically.

7. Turn the programmer switch to the automatic position, and the following sequence of events, which was discussed previously, takes place:

Step 1 -	zero	1 minute
2 -	total hydrocarbon analysis	5 minutes
3 -	zero	1 minute
4 -	methane analysis	5 minutes

This sequence is allowed to run as long as desired.

VIII. CALCULATIONS

At the end of the sampling period, the strip chart recording which contains data for both total hydrocarbons and methane is read by determining peak heights for each determination. The values of each THC determination and methane determination are averaged separately and compared to the calibration data. The difference between the two averages represents the non-methane hydrocarbons expressed in parts per million for that sampling period.

IX. RESULTS OF AMBIENT SAMPLING

The system shown in Figure 1 and already described has been in use in SwRI's mobile laboratory for about six months. Data were obtained near various industrial plants and in downtown Houston, usually close to point sources. Some of these data are shown in Table I. The sampling was done on a 4-6 hour sampling day, at which time methane was analyzed 50 percent of the time. The column was changed prior to each sampling day to insure reliability and confidence in the analysis. Occasional checks were made on the columns at the end of each sampling day with the aid of the prepared gas mixture and a gas chromatograph. To date, the columns have performed very satisfactorily.

Table I

COMPARISON OF DATA FOR TOTAL HYDROCARBONS, METHANE, AND NON-METHANE HYDROCARBONS

Continuous Sampling Vs. Composite Sampling Using Tedlar Sampling Bags

Date	Location	Upwind or Down	Total HC ppm		Methane ppm		Non-Methane HC ppm	
			Avrg. Cont.	Bag Samp.	Avrg. Cont.	Bag Samp.	Avrg. Cont.	Bag Samp.
Nov. 25, 1970	Plant A	DW	4.0	4.0	3.3	3.7	0.7	0.3
		DW	3.7	4.2	3.1	3.3	0.6	0.9
		UW	2.1	2.3	2.3	2.4	0.0	0.0
		UW	2.4	2.6	2.5	2.6	0.0	0.0
Dec. 9	Plant A	DW	3.3	4.0	1.4	1.7	1.9	2.3
		UW	1.3	1.7	1.2	1.2	0.1	0.5
		UW	1.8	2.2	1.6	1.5	0.2	0.7
Dec. 17	Plant A	DW	6.5	6.3	4.0	3.9	2.5	2.4
		DW	4.9	4.6	4.2	3.4	0.7	1.2
		UW	4.1	4.5	4.3	4.5	0.0	0.0
Feb. 9, 1971	Plant A	DW	6.4	6.2	5.9	5.8	0.5	0.4
		DW	5.3	5.4	5.5	5.3	0.0	0.1
		UW	5.0	5.0	5.1	5.0	0.0	0.0
		DW	5.3	5.4	5.3	5.2	0.0	0.2
Dec. 1, 1970	Plant B	DW	9.3	9.3	5.7	5.7	3.6	3.6
		DW	12.6	12.6	4.8	5.7	7.8	6.9
		UW	2.7	3.0	3.0	2.7	0.0	0.3
		DW	2.7	3.0	2.1	2.1	0.6	0.9
Jan. 7, 1971	Plant B	DW	4.8	4.8	3.4	3.4	1.4	1.4
		DW	10.9	11.9	3.4	3.6	7.5	8.3
		DW	3.1	3.4	2.8	2.6	0.3	0.8
		UW	2.3	2.4	2.2	2.2	0.1	0.2
Mar. 4	Plant B	DW	6.3	5.6	5.1	4.0	1.2	1.6
		DW	3.7	3.8	3.8	3.8	0.0	0.0
		DW	6.6	6.0	5.1	5.5	0.5	0.5
		UW	3.5	3.3	4.0	3.6	0.5	0.7

Table I (Continued)

Date	Location	Upwind or Down	Total HC ppm		Methane ppm		Non-Methane HC ppm	
			Avrg. Cont.	Bag Samp.	Avrg. Cont.	Bag Samp.	Avrg. Cont.	Bag Samp.
Dec. 20, 1970	Plant C	UW	5.6	5.2	5.6	5.2	0.0	0.0
		DW	6.9	6.4	5.4	5.4	1.5	1.0
Jan. 27, 1971	Plant C	DW	6.6	6.6	5.7	6.0	0.9	0.6
		DW	6.8	6.6	6.1	6.3	0.7	0.3
		DW	8.7	7.8	7.7	7.5	1.0	0.3
		UW	5.1	5.2	4.8	4.4	0.3	0.8
Feb. 10	Plant C	DW	2.8	3.0	2.1	2.2	0.7	0.8
		DW	2.7	2.6	2.7	2.6	0.0	0.0
		UW	6.0	6.4	6.5	6.4	0.0	0.0
		DW	8.6	8.4	7.7	7.8	0.9	0.6
Mar. 3	Plant C	DW	3.4	3.4	3.0	3.0	0.4	0.4
		DW	3.5	3.6	3.3	3.4	0.2	0.2
		UW	3.3	3.2	3.4	3.6	0.0	0.0
		DW	4.9	4.9	4.6	4.4	0.3	0.5
Mar. 10	Plant C	DW	4.1	4.1	3.9	3.9	0.2	0.5
		DW	3.7	4.0	3.7	4.0	0.0	0.0
		DW	4.9	4.3	4.5	4.4	0.4	0.0
Mar. 16	Houston (downtown area)	DW	6.3	6.5	6.0	6.0	0.3	0.5
		DW	7.3	8.5	7.6	8.7	0.0	0.0
		DW	7.7	8.4	8.4	9.0	0.0	0.0
		UW	7.8	7.8	8.2	8.1	0.0	0.0

X. ADDITIONAL SAMPLING RESULTS

In addition to obtaining continuous analytical data on methane and total hydrocarbons, simultaneous time-integrated samples were obtained also in Tedlar bags. The primary problem encountered in bag sampling was the tendency of plastic bags to desorb organic constituents that contaminated the sample. Tedlar was selected because this contamination was less with Tedlar than with other plastic materials, and even here exhaustive heating and purging was necessary prior to using a bag for this purpose. Frequent checks of background contamination with purified air were necessary to insure freedom from error due to this cause.

These bag samples were analyzed at the end of the sampling period, and the results compared with the averages of the continuous samples. The results of the THC and CH_4 in the sampling bags have generally compared very favorably with the averages of the continuous samples for each particular period of sampling as shown in Table I. Since the proposed federal standard requires the non-methane average for a period of three hours, the use of the sampling bag may be more practical. In this technique, it is unnecessary to change the charcoal scrubber column often, since the frequency of its usage is decreased tremendously.

XI. BIBLIOGRAPHY

Altshuller, A. P., Ortman, G. C., Saltzman, B. E., and Neligan, R. E., "Continuous Monitoring of Methane and Other Hydrocarbons in Urban Atmospheres," Journal of Air Pollution Control Association, 16:87-91 (1966).

Ortman, Gordon C., "Monitoring Methane in the Atmosphere With a Flame Ionization Detector," Analytical Chemistry, 38:644-646 (1966).

"Continuous Analysis of Methane," APCO, received by SwRI July, 1970, for evaluation (unpublished).

"Tentative Method for Continuous Measurement of Total Hydrocarbons in the Atmosphere" (Flame Ionization Method), SAC, received by SwRI February, 1971, for evaluation (unpublished).

APPENDIX

TOTAL HYDROCARBON AND METHANE ANALYZER

Operating Conditions

1.	Flow through carbon column	≈ 50-60 cc/min
2.	Flow through sample capillary	≈ 3 cc/min
3.	Flow through primary bypass	≈ 2 ℓ/min
4.	Flow through secondary bypass	≈ 50 cc/min
5.	Temperature	0° C

TOTAL HYDROCARBON AND METHANE ANALYZER

List of Suppliers

1. Four-Port Manual Selector Valves

   Circle Seal Model P4-418

   Distributor: Womack Machine Supply Company
   4006 Dennis - P. O. Box 88072
   Houston, Texas 77004

2. Solenoid Valves - Three-Port

   Asco "Red Hat"

   Cat. No. 832043

   Distributor: not available

3. Flowmeters

   Predictability: 0-10 ℓ/min Cat. No. 36-541-21
   0-84 cc/min Cat. No. 36-541-03

   Distributor: Greiner Scientific Corporation
   22 North More Street
   New York, New York 10013

4. Pressure Regulator

   Fisher Model 1-088 0-20 psig

   Distributor: Fisher Scientific Company
   P. O. Box 1307
   Houston, Texas 77001